

# PATENT SPECIFICATION

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NO DRAWINGS

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## (54) DYEING PROCESS

(71) We, I.W.S. NOMINEE COMPANY LIMITED, a British Company of Wool House, Carlton Gardens, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statements:—

This invention relates to an improved process for dyeing keratinous fibres.

Conventional dyeing processes usually entail heating the fibres with a solution of a dye to 80—100°C for periods of time which may in certain circumstances be prolonged. These processes have the disadvantage in that at the temperature at which they are carried out the fibres undergo a small degree of degradation as a result of which they tend to become yellow. This yellowness interacts with the colour of the dye to produce an unsatisfactory colour.

A process has been described of dyeing wool fibres comprising exhausting or padding a reactive dye on to the wool fibres at ambient or slightly elevated temperatures in the presence of urea, or other acid amides or thioamides. The temperatures at which this process is stated to be carried out are sufficiently low to prevent yellowing of the wool fibres. Nevertheless, this process suffers from the defect that when wool has been dyed and is then subjected to conventional water-fastness and perspiration tests, bleeding of the dye occurs which normally would indicate that the dye lacked fastness. We have discovered, however, that whilst during the dyeing process most of the dye becomes firmly bound to the wool fibres a proportion does not become so bound. Attempts were made to overcome this defect by removal of the unbound dye by washing.

This procedure was, however, found to be impractical in large scale dyeing processes. We have, however, made the further discovery that when wool fibres padded with reactive dyes in the presence of an acid amide or thio amide at pH 2—7 are subjected to an after-

treatment with either a reducing agent or a base, the portion of the dye which has not become firmly bound during the initial dyeing stage becomes firmly bonded to the fibres as a result of this after-treatment.

Accordingly, this invention provides a process for dyeing keratinous fibres which comprises impregnating the fibres at a pH value of 2—7, and a temperature of 10—60°C, with an aqueous composition containing a reactive dye and an acid amide or thio amide, storing the impregnated fibres in the presence of moisture to fix the bulk of the dye onto the fibres and thereafter treating the dyed fibres with an aqueous solution containing a reducing agent capable of breaking the disulphide bonds in the keratin molecule or a base.

The process can be applied to a wide variety of keratinous fibres, although the use of the wool of sheep is preferred. The wool can be in the form of alivers, loose fibres, rovings, slubbings, yarns and fabrics, whether in the form of piece goods or made-up garments. The wool may be natural or treated, e.g. shrink-proofed, oxidised or reduced.

The dyes that are used in the present process are reactive dyes, that is to say, those which react with the fibres and become attached to them by a covalent bond. The terms also include whitening agents which react with fibres in the same way. Dyestuffs falling within this class can incorporate the following groups:

epoxy-, ethylene-imino-, isocyanate, isothiocyanate, carbamic acid aryl-ester-, propiolic acid amide, mono-chloro-, and dichloro crotonylamino, chloroacrylamino-, acrylamino, sulpho halo-, sulphuric acid ester, sulphonyloxy-, labile halo atoms, trichloropyridazino-, dichloroquinoxalino-, allylsulphonyl-, and certain reactive ammonium or hydrazinium residues.

Especially good results are obtainable with highly reactive dyes, for example those incorporating a 2,4-dichlorotriazinyl, vinyl sul-

phenyl, 2,3-dichloroquinoxalino, or bromo-acrylamido group.

In the case of low-reactive halogen containing dyes, they may be rendered more reactive by applying them in admixture with a tertiary amine, for example triethylamine.

The process according to the invention is applicable to all forms of pad-dyeing. Padding is the application of a liquor or paste to fibres by passing them through the liquor or paste and subsequently through squeeze rollers, or by passing between squeeze rollers one of which carries the liquor or paste. A pad mangle is a convenient apparatus for carrying out this operation. An alternative impregnation technique is to saturate the fibres with the dye liquor and then remove excess liquor under a vacuum.

Various reducing agents can be used, and for the present purpose a reducing agent is a substance which is capable of breaking disulphide bonds in the keratin molecule. Suitable reducing agents include alkali metal, ammonium and amine sulphites and bisulphites, for example, sodium bisulphite, sodium meta bisulphite, and monoethanolamine bisulphite, certain quaternary phosphonium compounds, for example, tetrakis-(hydroxymethyl)-phosphonium chloride, sodium borohydride and thioglycolic acid. Various bases can be used which can comprise alkali metal or ammonium oxides and hydroxides, salts of strong bases and weak acids, for example, sodium bicarbonate, water-soluble aliphatic amines, for example dimethylamine. The reducing agents or bases are employed in the form of aqueous solutions which contain preferably 0.1 to 2.0% by weight of the dissolved material based on the weight of the solution. Ammonia is the preferred agent to use in the after-treatment step.

When producing shades on wool or similar materials by a method of impregnation followed by storage, it is accepted practice to add to the dye liquor a surfactant which produces rapid wetting of the wool at room temperature. These agents are exemplified by non-ionic condensation products of nonyl phenols with ethylene oxide to yield polyoxyethylated nonyl phenols containing from 10—30 moles of ethylene oxide, or by anionic alkyl sulphosuccinate derivatives. When hydrophilic dyes are used the addition of a surfactant is a preferred feature of the process if the best results are to be obtained.

In carrying out the initial dyeing process, the reactive dye is first dissolved or dispersed in water, and in the presence of an acid amide or thioamide, for example urea, thiourea, guanidine or their derivatives, but especially

at least 100 parts by weight urea per 1000 of the dye composition. The composition can be applied to the keratin fibres by conventional means, for example, by impregnating with a pad mangle. The process can be carried out at ambient temperatures, although slightly elevated temperatures preferably below 50°C, e.g. from 15 or 30 to 40°C, are best. Generally speaking, temperatures in the range 10 to 60°C are suitable. The dyeing can be carried out at a pH in the range 2—7 and most preferably at pH 3—6. The fibres are allowed to remain in contact with the dye for the minimum time for proper penetration, e.g. between 10 secs. and 72 hrs, typically between 1 and 24 hrs. The fibres may then be removed, squeezed to express excess liquid and then stored in the presence of moisture. The storage period is necessary for most dyeings and usually lasts from 10 mins. to 72 hrs; it ensures that the bulk of the dye is fixed to the keratinous fibres leading to a full shade development of the dye. After the storage period the fibres are treated with a solution of the reducing agent or the base for a period of preferably 5 to 15 mins. Conventional equipment can be used for applying these solutions, for example, a beam washer, a winch or a conventional washing range.

When this treatment has been effected, the dyed fibres are then dried and when subjected to conventional wash fastness tests, and perspiration tests, the dyes are found to display great fastness. This is in contrast to fibres which have been dyed by the process described above but in which the after-treatment with a reducing agent or base had been omitted. Fibres dyed according to this procedure displayed very poor fastness. This invention is illustrated by the following examples:

#### EXAMPLES 1—11

These examples illustrate the application of reactive dyes to wool materials by means of a padding process. All the processes were carried out at 20°C. The following procedure was adopted in each case. 100 parts of wool material were immersed for 60 secs. in an aqueous dye liquor at 20°C having the composition indicated below. The material was then squeezed between rollers to a total weight of 200 parts and stored for up to 48 hrs. at room temperature under conditions which prevented drying. The material was then well rinsed in cold water, and subjected to an after-treatment with a dilute solution of the specified base or reducing agent in a winch for a period of 15 mins. Finally the material was rinsed with water to neutrality, hydro-extracted and dried.

Example No.	Material	Dye	Agents	Storage Time	Base or Reducing Agent	Result
1	SDC Serge	Procion Brill. Red M-5B 10 parts per 1,000 parts of liquor	10 parts Aerosol OT per 1,000 of liquor Acetic Acid—pH <sub>4</sub> . Urea 150 parts per 1,000 of liquor	48 hrs.	Ammonia 1.0% v/v solution at 40°C.	Very fast, bright level shade
2	Doctor Flannel (Loomstate)	Procion Blue M-3Gq 20 parts per 1,000 of liquor	Aerosol OT 10 parts per 1,000 of liquor Acetic Acid—pH <sub>5</sub> . Urea 300 parts per 1,000 of liquor.	24 hrs.	Sodium bisulphite 1% solution at 40°C.	Very fast, level shade
3	Slubbings	"	"	"	Ammonia 0.1% v/v solution at 60°C.	"
4	Doctor Flannel (Loomstate)	Levafix Brill. Blue P-RL 10 parts per 1,000 liquor	Aerosol OT 10 parts per 1,000 of liquor Formic acid—pH <sub>5</sub> . Urea 300 parts per 1,000 of liquor.	24 hrs.	Ammonia 0.1% v/v solution at 60°C.	Very fast, bright level shade
5	Doctor Flannel (Bleached)	Ramazol Brill. Blue R 2 parts per 1,000 liquor (activated to vinyl sulphone)	Aerosol OT 10 parts per 1,000 of liquor Acetic Acid—pH <sub>6</sub> . Urea 100 parts per 1,000 of liquor	5 hrs.	Thioglycollic acid, 1% solution at 40°C.	Fast, bright level shade

Example No.	Material	Dye	Agents	Storage Time	Base or Reducing Agent	Result
6	Doctor Flannel (Bleached)	Bis - 4,4' - (2 chloro-4-morpholino - 1,3,5, tri-aziny) (6) - diamino stilbene - 2,2' - disulphonic acid to 10 parts per 1,000 of liquor.	Aerosol OT 10 parts per 1,000 of liquor Acetic Acid—pH5 Urea 300	24 hrs.	Terakis—(hydroxymethyl phosphonium chloride, 0.1% v/v solution Room temperature	Very fast, bright, level, fluorescent whitening produced.
7	S.D.C. Serge	Procion Red M—G 10 parts per 1,000 parts liquor.	Lissapol N 10 parts per 1,000 parts liquor. Urea 300 parts per 1,000 parts of liquor. Acetic Acid—pH5.	24 hrs.	Ammonia 0.1% v/v 40°C.	Fixation measured as 80% before after-treatment and 98% when after-treated.
8	S.D.C. Serge	Procion Brill.Red H—3BN (low reactive type)	Urea 300 parts per 1,000 parts of liquor Lissapol N10 parts per 1,000 parts of liquor. Acetic Acid—pH 5.	48 hrs.	0.1% NN-dimethyl hydrazine 0.1% NH <sub>3</sub> solution	Much greater fastness to wet treatments than if NN, dimethyl hydrazine omitted.

Example No.	Material	Dye	Agents	Storage Time	Base or Reducing Agent	Result
9	Double Jersey knitted fabric	Reactofil Brilliant Red 2B (Geigy) 20 parts per 1,000 parts liquor	Lissapol N 10 parts per 1,000 parts liquor, Urea 300 parts per 1,000 parts liquor, Acetic Acid to pH 5.	48 hrs.	Sodium Bicarbonate 0.1% v/v solution 40°C.	Very fast, level dyeing. Fixation measured before after-treatment is 70% after the after-treatment 87%
10	Chlorinated wool serge.	Precision Turquoise Blue H-A 10 parts per 1,000 parts liquor.	Lissapol N 10 parts per 1,000 parts liquor, Urea 300 parts per 1,000 parts liquor, Acetic acid at pH 5.	48 hrs.	Monoethanolamine Sulphite	Very fast, level dyeing.
11	Serge.	Precision Red MG 20 parts per 1,000 parts liquor.	Lissapol N 10 parts to 1,000 parts liquor, Urea 300 parts to 1,000 parts liquor, Acetic Acid pH 5.	48 hrs.	Dimethylamine	A fast level dyeing Dye fixation 76% before after-treatment and 90% when after-treated.

In those Examples where fixation results are given, these values were measured according to the method of Hadfield and Lemin, *Journal Textile Institute* 51, (1960) T 1351, where the dyeing is subjected to repeated strippings with an aqueous solution containing 50% urea and 1% of a surfactant until the final extract is colourless. The extracts are combined and determined spectrophotometrically. In examples 9 and 13 urea was replaced by 25% aqueous pyridine in the stripping solution.

## WHAT WE CLAIM IS:—

1. A process for dyeing keratinous fibres which comprises impregnating the fibres at a pH value of 2—7 and a temperature of 10—60°C, with an aqueous composition containing a reactive dye and an acid or thio amide, storing the impregnated fibres in the presence of moisture to fix the bulk of the dye onto the fibres and thereafter treating the dyed fibres with an aqueous solution containing a reducing agent capable of breaking the disulphide bonds in the keratin molecule or a base.
2. A process as claimed in Claim 1 wherein the aqueous solution contains 0.1 to 2.0% by weight of the reducing agent or base.
3. A process as claimed in Claim 1 or 2 wherein the aqueous solution contains an alkali metal, ammonium or amine sulphite or bisulphite.
4. A process as claimed in Claim 1 or 2 wherein the aqueous solution contains an alkali metal hydroxide, a salt of a weak acid and a strong base, or a water-soluble aliphatic amine.
5. A process as claimed in Claim 1 or 2 wherein the aqueous solution contains ammonia.
6. A process as claimed in any one of the preceding claims wherein the aqueous composition contains a surfactant.
7. A process as claimed in any one of the preceding claims wherein at least 100 parts by

weight urea is present in 1000 parts by weight of the aqueous composition.

8. A process as claimed in any preceding claim wherein the keratinous fibres are in the form of a wool fabric.

9. A process as claimed in any one of the preceding claims wherein the impregnated fibres are stored for a period of 1 to 48 hrs. to fix the bulk of the dye on the keratinous fibres.

10. A process as claimed in any preceding claim wherein the temperature of the aqueous composition is from room temperature to 40°C.

11. A process according to any preceding claim in which the dye is one which incorporates a 2,4-dichloro-triazinyl, vinyl sulphonyl, 2,3-dichloroquinoxalino, or bromo-acrylamido group.

12. A process for dyeing keratinous fibres substantially as hereinbefore described with reference to Examples 1 to 6.

13. A process for dyeing keratinous fibres substantially as hereinbefore described with reference to Examples 7 to 11.

14. Keratinous fibres whenever treated by a process claimed in any one of the preceding claims.

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